

Resonant Inelastic X-ray Scattering Study of the Organic Semiconductor TDATA.

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Beamline(s): X1B

Introduction: The organic semiconductor 4, 4', 4''-tris(diphenylamino)triphenylamine (TDATA) (see diagram below) has recently been used as a matrix host in organic light emitting diode (OLED) construction. The chemically simple structure of the material provides an excellent opportunity to demonstrate the potential of RIXS in the investigation of the site specific electronic structure of organic materials.

Methods and Materials: Thin film samples were prepared in-situ via organic molecular beam deposition (OMBE) on Si(100) substrates. The polycrystalline films were deposited at a base pressure of 8×10^{-9} torr and a substrate temperature of 353K. Previously observed problems with beam damage to the sample structure, were avoided through a combination of a small beam spot size and sample translation scheme. The local valence band (VB) electronic structure at C sites in the structure was investigated via resonant soft x-ray emission spectroscopy at the C 1s edge. Chemically the C sites in the structure can be grouped into two sets, those that are neighboring N atoms and those that are not. In this experiment soft x-ray photons are used to selectively generate C1s core level vacancies (via $1s \rightarrow \pi^*$ transitions) at each of the two types of chemical sites. The spectrum of x-rays emitted as the core hole decays represents the site local VB PDOS modified by orbital symmetry conservation requirements.

Results: Presented in figure 1 is the C 1s XAS spectrum of TDATA. Peak A represents C1s \rightarrow LUMO (π^*) transitions, whereas peak B is a result of chemically shifted C1s states in an environment modified by the presence of a neighboring N atom. Small features at C & D represent transitions to LUMO+1 states. Figure 2 presents RIXS spectra for each of the excitation energies A through D indicated in figure 1. The peak on the right hand side of each plot is produced by elastically scattered light. Spectrum A strongly resembles that produced by benzene, indicating that the basic electronic structure and symmetry of the benzene ring is preserved in TDATA. The differences seen in spectrum B are produced by modification to the local electronic environment of the C by its neighboring N atom, which breaks the symmetry of the benzene ring, partially allowing transitions that were previously disallowed. The fact that the changes are relatively small indicates that the de-localized π electron structure of the benzene molecule is preserved and continues across the -N= bridge. Spectra C & D further support this conclusion.

Conclusions: RIXS was used to investigate the C 1s site specific electronic structure of the wide band organic semiconductor TDATA. It was found that while the orbital symmetry and π electron structure of the material closely resembles that of benzene, several features are introduced by the symmetry breaking -N= bridge structure.

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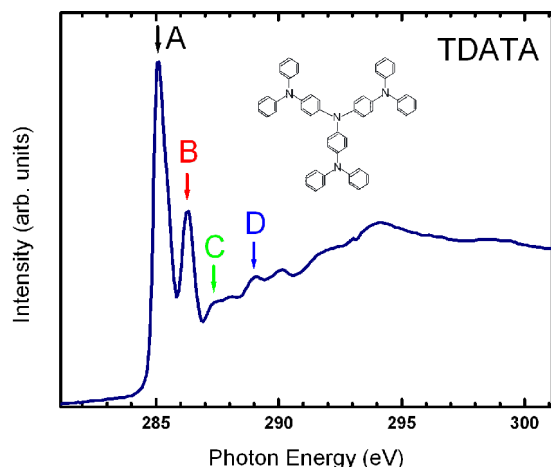


Figure 1. C 1s XAS spectrum for TDATA.

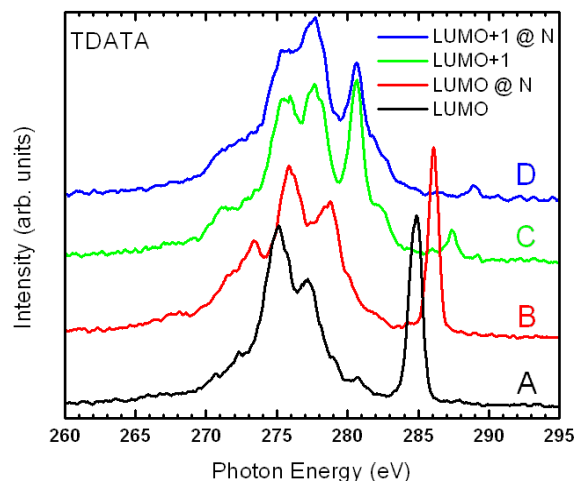


Figure 2. C 1s RIXS spectra for incident photon energies corresponding to C 1s to LUMO, LUMO near N, LUMO+1 and LUMO+1 near N resonant transitions.